

Figure 3. Another view of the molecule in the direction from C(3) to C(6).

between the two bridged carbons ( $sp^3$ ) has been observed. In the present molecule, there is no lengthening of the bridging  $C(sp^2)=C(sp^2)$  aromatic bond whereas appreciable angle deformation of  $\angle C(11)-C(1)-C(2)$  and  $\angle C(21)-C(2)-C(1)$  of average  $116.4(5)^\circ$  from  $120^\circ$  for the normal  $sp^2$  carbon emerges. The angle  $\varphi$  defined (in Table V) by the plane of ring 1 (or 2) and the bond  $C(11)-C(1)$  (or  $C(21)-C(2)$ ) is  $14.9^\circ$ . The C-C bond distances in rings 1 and 2 range from  $1.411(10)$  to  $1.441(7)$  Å (average  $1.432(12)$  Å) and from  $1.401(10)$  to  $1.443(8)$  Å (average  $1.429(16)$  Å), respectively. These average values may be compared with the accepted C-C ( $\pi$ -cyclopentadienyl) bond length of  $\sim 1.43$  Å. The C-H bond distances in rings 1 and 2 range from  $0.96(5)$  to  $1.23(8)$  Å (average  $1.09(6)$  Å).

Other bond distances and angles involving ring C are noticeably symmetrical about the line bisecting the central benzene through the Fe atom: The bond distances  $C(2)-C(3)$  and  $C(6)-C(1)$  are  $1.402(7)$  and  $1.404(6)$  Å,  $C(3)-C(4)$  and  $C(5)-C(6)$  are  $1.425(7)$  and  $1.421(7)$  Å, and  $C(4)-C(5)$  is  $1.400(9)$  Å (average  $1.407(14)$  Å, which agrees with the accepted value of  $1.395(3)$  Å for the benzene ring 7). It would be noteworthy that the bond  $C(1)-C(2)$  is the shortest and the difference between the distances  $C(3)-C(4)$  and  $C(1)-C(2)$  is  $>3\sigma$ , although the difference may not be significant because similar but not so systematic deviations as in the present molecule in bond lengths and angles have been shown in hexaphenylbenzene.<sup>12</sup>

Registry No. 3a, 61332-68-1.

Supplementary Material Available: Listings of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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- (5) The absorption correction program ABS10 (by T. Ito) used the Gaussian integration method of Busing and Levy. The following programs were used during the course of the structural analyses: FANDFR, structure factor calculation and Fourier synthesis, Y. Iitaka; HBLS, structure factor calculation and block-diagonal least-squares refinement, T. Ashida; BOND, distances, angles, and least-squares planes, Y. Iitaka; ORTEP, thermal ellipsoid drawings, C. K. Johnson.
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## Studies in Heavy-Metal Molybdates. 2. Crystal Structure of Disodium Di- $\mu$ -hydroxo-dizinc(II) Molybdate

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Received September 7, 1976

AIC60660M

Sodium  $\mu$ -hydroxo- $\mu$ -aquo-dizinc(II) molybdate,  $\text{NaZn}_2(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$ , was found to form a compound of composition  $\text{NaZn}(\text{OH})\text{MoO}_4$  when allowed to react in a pressure bomb with 4 M sodium molybdate. The crystals are orthorhombic with  $a = 7.850(1)$ ,  $b = 9.2922(8)$ ,  $c = 6.148(1)$  Å, and  $V = 444.4$  Å<sup>3</sup>. Systematic absences fixed the space group as  $Pna2_1$ . The density, determined by flotation in a thalious formate-thalious malonate solution, was  $\sim 4$  g cm<sup>-3</sup> compared to a calculated density with  $Z = 4$  of  $3.965$  g cm<sup>-3</sup>. A total of 843 intensities above background were collected by counter diffractometry using the  $\theta$ - $2\theta$  scan technique. The structure was solved by a combination of Patterson and Fourier methods. Refinement by block-diagonal least-squares procedures led to a final  $R_F$  of 0.038 and a weighted residual  $R_{wF}$  of 0.036. The zinc atoms are octahedrally coordinated by oxygen atoms which share edges forming infinite chains of octahedra. These chains are linked by molybdate tetrahedra to form zinc molybdate sheets. The sheets are not separated by sodium ions as in  $\text{NaZn}_2(\text{OH})(\text{H}_2\text{O})\text{MoO}_4$  but are interconnected through both molybdate groups and sodium ions. The hydrogen atom was placed on the oxygen which bridges zinc atoms based upon electrostatic bond strength considerations. This made the structure a disodium di- $\mu$ -hydroxo-dizinc(II) molybdate.

### Introduction

Pezerat has reported that at least three well-defined phases can be obtained from the reaction of a soluble zinc salt with sodium molybdate.<sup>2</sup> Two of the phases are sodium zinc molybdates designated by him as  $\Phi_x$  and  $\Phi_y$ . The crystal

structure of the  $\Phi_x$  phase was reported upon in paper 1 of this series.<sup>3</sup> It has the composition  $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ . We have now isolated single crystals of phase  $\Phi_y$  and its structure is reported upon here.

Phase  $\Phi_y$  was described by Pezerat as having the ideal

Table I. Final Positional and Anisotropic Thermal Parameters<sup>a,b</sup>

Atom	x	y	z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
Zn	0.504 3 (7)	0.000 4 (1)	0.4146 (13)	44 (2)	38.7 (8)	44 (2)	16 (3)	8 (4)	-5(4),
Mo	0.123 88 (9)	0.170 61 (7)	0.1591 (8)	26.2 (6)	22.6 (4)	54 (1)	9.6 (15)	-3.8 (13)	5 (10)
Na	0.363 7 (7)	0.310 4 (4)	0.6580 (30)	130 (9)	42 (5)	162 (13)	-8 (11)	111 (66)	-65 (48)
O(1)	0.110 6 (9)	0.276 9 (5)	-0.0831 (10)	85 (10)	27 (5)	10 (10)	88 (44)	19 (28)	3 (13)
O(2)	0.118 3 (18)	0.282 9 (12)	0.3713 (20)	223 (29)	176 (20)	428 (58)	-94 (42)	276 (93)	141 (49)
O(3)	0.449 4 (11)	0.446 5 (11)	0.1564 (20)	141 (20)	182 (17)	551 (56)	40 (25)	228 (83)	-474 (25)
O(4)	0.871 3 (9)	0.435 5 (5)	0.6509 (20)	73 (10)	60 (6)	66 (22)	-5 (15)	-100 (80)	-2 (60)
O(5)	0.308 2 (9)	0.063 6 (6)	0.1478 (22)	98 (12)	91 (8)	97 (36)	89 (15)	88 (55)	-87 (45)

<sup>a</sup> Estimated standard deviations in parentheses are right-adjusted to the last digits of the preceding number and are derived from the inverse of the final least-squares matrix. <sup>b</sup> Thermal parameters in  $\text{Å}^2$  are of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)] \times 10^4$ .

compositions  $\text{Na}_2\text{Zn}_2\text{H}_2\text{Mo}_2\text{O}_{10}$  or  $\text{Na}_{2-x}(\text{H}_2\text{O})_x\text{Zn}_2\text{Mo}_2\text{O}_9$ .<sup>2,4</sup> Weissenberg photographs of very small (50–100  $\mu$ ) crystals revealed rhombohedral symmetry with cell dimensions, based upon a hexagonal cell, of  $a = 6.113 \text{ \AA}$  and  $c = 21.80 \text{ \AA}$  for the ammonium salt.<sup>4,5</sup> The actual compositions differed somewhat from the ideal and the structure was found to be disordered. Several difficulties in completing the structure were encountered by Pezerat. Deficiencies of zinc and molybdenum were accounted for by invoking cation vacancies. However, in order to achieve charge and mass balances it was necessary to postulate the presence of neutral water and/or ammonia molecules. Since only 147 reflections were available and the refinement appeared to be incomplete ( $R = 0.09$ ), many questions concerning this structure remain unanswered. Therefore, it was felt that a redetermination was in order.

### Experimental Section

**Preparation.** Sodium zinc molybdate (phase  $\Phi_x$ ), prepared as described in paper 1,<sup>3</sup> was added to a 4 M sodium molybdate solution in the proportions of 1 g/10 ml. This mixture was placed inside a Teflon-lined stainless steel Parr general-purpose bomb (Parr Instrument Co.) and held at 220–230 °C for 3 weeks. A powder pattern of the resultant solid showed that it was a mixture of the original sodium zinc molybdate and a second phase. Single crystals were separated from the solid mass by hand picking with the aid of a microscope. In this manner about half a dozen crystals of the subject compound were isolated. No elemental analysis was carried out due to the very small amount of pure material available.

**Crystal Data.** The crystal shape approximated a rectangular parallelepiped with dimensions 0.08 mm  $\times$  0.06 mm  $\times$  0.1 mm. It was mounted with the long direction parallel to the  $\phi$  axis of a CAD-4 (Enraf-Nonius) four-circle counter diffractometer and an orientation matrix was found with the aid of program SEARCH.<sup>6</sup> The experimental conditions as well as the method of data collection and the derivation of accurate unit cell dimensions were as described previously.<sup>3</sup> The unit cell was found to be orthorhombic with  $a = 7.850 (1) \text{ \AA}$ ,  $b = 9.2922 (8) \text{ \AA}$ ,  $c = 6.148 (1) \text{ \AA}$ , and  $V = 444.4 \text{ \AA}^3$ . The density, determined (only with difficulty) by flotation in a thallos formate-thallos malonate solution, was found to be  $\sim 4 \text{ g cm}^{-3}$ . This compares to a calculated density of  $3.965 \text{ g cm}^{-3}$ . A scan of several hundred reflections in all zones revealed the following systematic absences:  $h0l$  for  $h = 2n + 1$ ,  $0kl$  for  $k + l = 2n + 1$ ,  $h00$  for  $h = 2n + 1$ ,  $0k0$  for  $k = 2n + 1$ , and  $00l$  for  $l = 2n + 1$ . These absences fix the space group unequivocally as  $Pna2_1$ . Assuming a formula weight of 265.3 g for the suspected composition  $\text{NaHZnOMoO}_4$ , there are then four formula units per unit cell.

Intensity data were collected with monochromated (graphite crystal) Mo  $K\alpha$  radiation ( $\lambda 0.7107 \text{ \AA}$ ) at a  $4^\circ$  takeoff angle. The scan width was  $3(0.7 + 0.2 \tan \theta)^\circ$ . Scans of sets of equivalent reflections showed agreement within  $\pm 5\%$ . During data collection two standard reflections were recorded every 24 reflections and these were used to place all of the intensity data on a common scale. The variation in intensities of the standards was small and random, with maximum fluctuation about the mean of  $\pm 4\%$ . A total of 2136 reflections were scanned out to a maximum  $2\theta$  angle of  $80^\circ$ . Of these, 843 had intensities with  $I \geq 3\sigma(I)$  where  $\sigma(I) = [\text{TOT CTS} + \text{BKGD CTS}]^{1/2}$  and therefore were considered to be observed.

The data were corrected for Lorentz and double-polarization effects but not for absorption or extinction. Because of the small size and nearly equisidedness of the crystal ( $\mu_r = 0.66$  average) the absorption

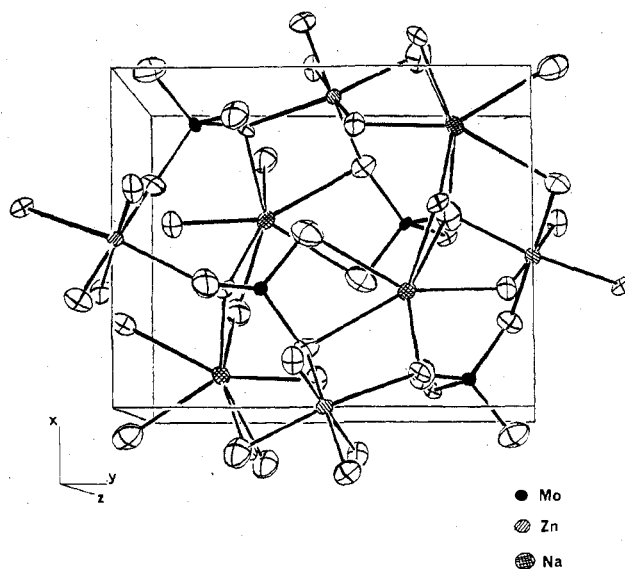


Figure 1. Portion of the unit cell as drawn by ORTEP.<sup>12</sup>

error was expected to be negligible.

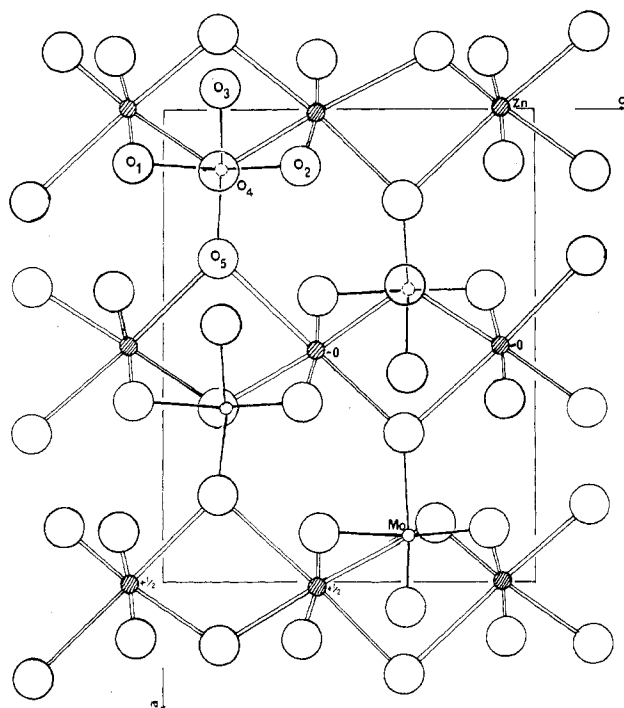
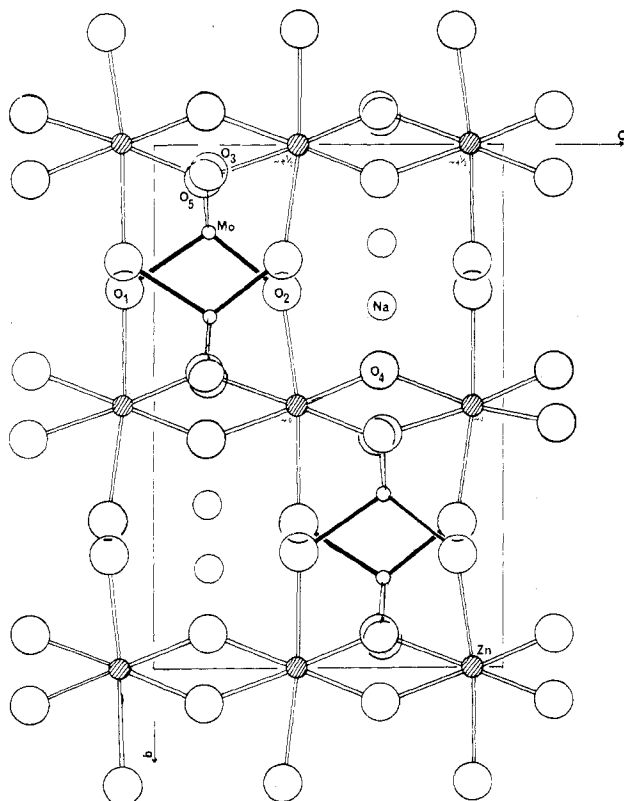
### Solution and Refinement of the Structure

A three-dimensional Patterson map was prepared from which the positions of the heavy-metal atoms were readily obtained. The positions of the other nonhydrogen atoms were then derived from successive Fourier and difference maps. These maps clearly showed that the proportion of sodium to zinc was unity. Refinement of the positional and isotropic temperature factors by the block-diagonal method<sup>7</sup> gave a reliability index,  $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ , of 0.052. A difference map showed that the atoms were undergoing slight anisotropic thermal motion. Therefore refinement was continued with allowance for this motion until changes in the thermal and positional parameters were equal to or less than one-tenth of their respective standard deviations. The final values of  $R_F$  and of the weighted reliability index,  $R_{wF} = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ , were 0.038 and 0.036, respectively. The function minimized was  $\sum w(|F_o| - |F_c|)^2$  with weights assigned according to the expression  $w = 1 / \{1 + [(|F_o| - P_2) / P_1]^2\}$  where the final values of  $P_1$  and  $P_2$  were 30 and 95, respectively.

Ionic scattering factors were assigned ( $F^-$  was used in place of  $O^{2-}$ ) in the same way as described for sodium zinc molybdate(I).<sup>3</sup> The final positional and thermal parameters are given in Table I. A table of observed and calculated structure factors is available.<sup>8</sup> Unobserved reflections were assigned a threshold value which was slightly less than the value of the weakest observed reflection in the same angular range. About 4% of the unobserved reflections were found to be slightly above threshold. Comparison of the  $F_o$  and  $F_c$  values for low-angle reflections indicated no appreciable lowering of the intensities due to extinction. A final difference synthesis revealed termination of series ripples about the heavy elements and a number of regions of positive density, ranging from 0.3 to  $0.9 \text{ e/\AA}^3$ , randomly distributed. None of these peaks could be attributed to the positions of hydrogen atoms.

### Description of the Structure

A portion of the unit cell contents is shown in Figure 1 and projections of the unit cell onto the  $xz$  and  $yz$  planes are shown

Figure 2. Projection of the unit cell onto the  $xz$  plane.Figure 3. Projection of the unit cell onto the  $yz$  plane.

in Figures 2 and 3, respectively. The zinc atoms are octahedrally coordinated by oxygen atoms and the octahedra share edges. This produces chains of octahedra very nearly centered at  $1/2x$  and  $1/2y$  running parallel to the  $c$  direction. This is clearly seen in the projections. The chains are linked to each other through tetrahedral molybdate groups each of which share three corners with the octahedra. The shared oxygens are O(1), O(2), and O(5). Since there are two O(5) atoms in each octahedron, four octahedral corners are shared with

Table II. Interatomic Distances (Å)

A. Zinc-Oxygen Octahedra <sup>a</sup>			
Zn-O(1)	2.264 (11)	Zn-O(4)(d)	1.882 (14)
Zn-O(2)	2.219 (15)	Zn-O(5)(a)	2.325 (13)
Zn-O(4)(c)	1.988 (14)	Zn-O(5)(b)	2.135 (13)
B. Molybdenum-Oxygen Tetrahedra			
Mo-O(1)	1.790 (7)	Mo-O(3)	1.747 (9)
Mo-O(2)	1.669 (13)	Mo-O(5)	1.755 (7)
C. Sodium-Oxygen Polyhedron			
Na-O(1)(a)	2.562 (15)	Na-O(3)(b)	2.692 (10)
Na-O(1)(d)	2.633 (15)	Na-O(4)(d)	2.360 (6)
Na-O(2)(a)	2.623 (19)	Na-O(5)(c)	2.712 (13)
Na-O(2)(d)	2.799 (20)		

<sup>a</sup> In this table and Table III the parenthesized letter in the identifying symbols for the atoms refers to the symmetry related positions as follows: (a)  $x, y, z$ ; (b)  $\bar{x}, \bar{y}, \bar{z} + 1/2$ ; (c)  $1/2 - x, 1/2 + y, 1/2 + z$ ; (d)  $1/2 + x, 1/2 - y, z$ .

Table III. Interatomic Angles (deg)

Atoms	Angle	O-O Contact (Å)
A. Molybdenum-Oxygen Tetrahedra		
O(1)-Mo-O(2)	107.6 (5)	2.793
O(1)-Mo-O(3)	106.8 (6)	2.841
O(1)-Mo-O(5)	109.1 (4)	2.888
O(2)-Mo-O(3)	112.1 (7)	2.835
O(2)-Mo-O(5)	114.0 (5)	2.873
O(3)-Mo-O(5)	106.9 (6)	2.813
B. Zinc-Oxygen Octahedra		
O(5)(a)-Zn-O(1)(c)	88.4 (4)	3.200
O(5)(a)-Zn-O(2)(d)	87.2 (5)	3.135
O(5)(a)-Zn-O(4)(c)	79.9 (5)	2.780
O(5)(a)-Zn-O(4)(d)	95.6 (5)	3.131
O(5)(a)-Zn-O(5)(b)	177.0 (5)	
O(5)(b)-Zn-O(1)(c)	90.9 (4)	3.135
O(5)(b)-Zn-O(2)(d)	93.3 (5)	3.166
O(5)(b)-Zn-O(4)(c)	97.2 (5)	3.093
O(5)(b)-Zn-O(4)(d)	87.3 (5)	2.780
O(4)(c)-Zn-O(1)(c)	85.4 (4)	2.892
O(4)(c)-Zn-O(2)(d)	88.8 (5)	2.948
O(4)(d)-Zn-O(1)(c)	93.8 (5)	3.039
O(4)(d)-Zn-O(2)(d)	91.7 (5)	2.951
O(2)(d)-Zn-O(1)(c)	173.3 (5)	
C. Sodium-Oxygen Polyhedron		
O(1)(a)-Na-O(1)(d)	99.0 (5)	
O(1)(a)-Na-O(2)(a)	80.6 (5)	
O(1)(a)-Na-O(2)(d)	154.8 (6)	
O(1)(a)-Na-O(3)(d)	121.7 (6)	
O(1)(a)-Na-O(4)(d)	84.9 (5)	
O(1)(a)-Na-O(5)(c)	74.7 (4)	
O(1)(d)-Na-O(2)(a)	156.3 (6)	
O(1)(d)-Na-O(2)(d)	76.2 (4)	
O(1)(d)-Na-O(3)(b)	82.0 (5)	
O(1)(d)-Na-O(4)(d)	71.6 (5)	
O(1)(d)-Na-O(5)(c)	130.3 (5)	
O(2)(a)-Na-O(2)(d)	94.0 (5)	
O(2)(a)-Na-O(3)(b)	118.6 (6)	
O(2)(a)-Na-O(4)(d)	84.8 (5)	
O(2)(a)-Na-O(5)(c)	72.8 (5)	
O(2)(d)-Na-O(3)(b)	82.5 (5)	
O(2)(d)-Na-O(4)(d)	70.1 (5)	
O(2)(d)-Na-O(5)(c)	127.5 (6)	
O(3)(b)-Na-O(4)(d)	145.5 (7)	
O(3)(b)-Na-O(5)(c)	62.8 (5)	
O(4)(d)-Na-O(5)(c)	151.6 (6)	

four different molybdate tetrahedra. The oxygens involved in sharing corners with the molybdate groups also are the ones which form the four long Zn-O bonds (Table II). This linkage of octahedra by tetrahedra is quite similar to that in  $\text{NaZn}_2(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$ .<sup>3</sup> In this latter structure the sharing is such as to create zinc molybdate layers parallel to the  $xy$  plane. Similar layers exist in the present structure but the layers run parallel to  $c$ , diagonally cutting the axes at  $1/2a$  and  $1/2b$ , i.e., the 220 plane. However, in the present structure adjacent layers are connected to each other through molybdate

tetrahedra whereas in  $\text{NaZn}(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$  the layers are separated by sodium ions.

Sodium ions are at roughly  $1/3$ ,  $1/3$ ,  $2/3$  and have seven oxygen near neighbors with interatomic distances (Table II) ranging from 2.360 to 2.799 Å. The coordination may be viewed as octahedral with the seventh oxygen near the center of one of the octahedral faces. Oxygens 1 and 2 are each shared between two sodium ions forming zigzag chains of sodium-oxygen polyhedra.

**Assignment of Hydrogen Atoms.** In order to achieve charge balance one unique hydrogen must be placed in the structure. Each O(2) is bonded to two sodiums, one zinc, and one molybdenum atom. Likewise O(5) is four-coordinate being bonded to two zincs, one sodium, and one molybdenum atom. Thus, it is unlikely that these oxygens are involved in hydrogen bonding. On the other hand O(3) has only two near neighbors (Mo and Na) and O(4) is three-coordinate (two zincs and one sodium). The interatomic distance O(3)(a)-O(4)(b) is 2.743 (11) Å. Other short contacts are O(4)-O(5), 2.780 Å, which arises from bridging of the zinc atoms and O(3)(a)-O(5)(d), 2.813 (12) Å.

Pauling has shown that the electrostatic bond strength (EBS) received by an anion (in minerals) from all of the cations to which it is bonded rarely differs by more than  $\pm 1/16$  of its formal charge.<sup>9</sup> This rule can be used to help to decide which oxygens are involved in hydrogen bonding. The strengths of the bonds from metal to oxygen are  $3/2$  for Mo,  $1/3$  for Zn, and  $1/6$  for  $\text{Na}^+$ . This last value is used for sodium rather than the more correct one of  $1/7$  to avoid unduly large common denominators. As will be seen, its use does not effect the argument. We shall also adhere to Baur's suggestion that for each hydrogen bond  $5/6$  of the bond strength is assigned to the donor and  $1/6$  to the acceptor.<sup>10</sup> Considering O(3) as donor and O(4) as acceptor yields EBS values of  $2^{1/2}$  and 1, respectively, for these two atoms. However, if the reverse were true, the EBS's are  $1^{5/6}$  and  $1^{2/3}$ . According to Baur the lengths of hydrogen bonds formed between pairs of anions vary inversely as the difference in the electrostatic bond strengths of the donor and acceptor.<sup>11</sup> The predicted O-O distance for an EBS difference of  $-1/6$  is  $\sim 2.9$  Å which is close to the observed O(3)-O(4) contact distance. All other combinations of hydrogen bonding involving oxygens with short O-O contacts lead to unreasonable results. Placing the hydrogen on O(4) makes the formula  $\text{NaZn}(\text{OH})(\text{MoO}_4)_2$ .

#### Discussion

The zinc-oxygen octahedra are somewhat distorted relative to those in  $\text{NaZn}_2(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$ . This distortion arises

from the very short Zn-O(4) bonds and significantly longer Zn-O(5) distances which form the equatorial plane of the octahedron. Again Bauer has shown<sup>11</sup> that bond lengths generally increase with increasing EBS of the anion in ionic and partly ionic compounds. In the present case O(5) has the largest EBS and O(4) the smallest so the bond lengths conform to the above rule. The somewhat short Zn-O(5)(b) bond, which does not fit the EBS requirement, may result from the structure's avoidance of too great a distortion which would follow from another overly large Zn-O equatorial bond. In spite of the large range for the zinc-oxygen bond distances, the average, 2.14 (17) Å, is close to that expected for this bond.<sup>3</sup>

The present structure is completely different from the one reported by Pezerat for phase  $\Phi_y$ .<sup>2,4</sup> The rhombohedral cell reported by Pezerat was obtained on nonstoichiometric products while our preparation is stoichiometric. Sufficient differences in composition may exist to bring about phase changes and this point will be investigated.

The present structure can be thought to arise from  $\text{NaZn}_2(\text{OH})(\text{H}_2\text{O})(\text{MoO}_4)_2$  by replacement of one of the water protons by a sodium ion. One of the two aquo protons was found to be disordered, being statistically distributed among the two zinc hydroxyl groups.<sup>3</sup> This proton is probably more acidic than the others and thus in a more basic medium is replaced by sodium ion to form disodium di- $\mu$ -hydroxo-dizinc molybdate,  $\text{Na}_2\text{Zn}_2(\text{OH})_2(\text{MoO}_4)_2$ .

**Registry No.**  $\text{NaZn}(\text{OH})(\text{MoO}_4)$ , 61231-78-5;  $\text{NaZn}_2\text{OH}(\text{H}_2\text{O})(\text{MoO}_4)_2$ , 57606-42-5.

**Supplementary Material Available:** Listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

#### References and Notes

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